Studies on the Dephosphorization of Liquid Iron : Effect of Phosphorous on the Activity of Oxygen in Liquid Iron

Studies on the Dephosphorization of Liquid Iron. Effect of Phosphorous on the Activity of Oxygen in Liquid Iron*

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Synopsis

The interaction between oxygen and phosphorous in liquid iron was studied by the method of equilibrating liquid iron-phosphorous alloys with hydrogen/water-vapor mixtures (of a given composition). The composition of gas mixture was so determined that slag was not formed. In order to examine the effect of temperature on the interaction parameter $e_0^{(P)}$, experiments were performed at three different temperatures, 1540°C, 1585°C and 1625°C; but there was hardly any difference within the experimental errors.

The interaction parameter $e_0^{(P)}$ ($=\partial \log f_0^{(P)}/\partial[\%P]$) calculated from the present results was approximately +0.06 at an average temperature 1585°C.

I. Introduction

Hitherto, many works have been done on the dephosphorizing reaction in the steelmaking process, and the recent development of top-blown converters has thrown the behavior of phosphorous in steelmaking process into greater attention.

In this report, the authors present the experimental results on the effect of phosphorous on the activity of oxygen in liquid iron, with the aim of obtaining fundamental data on the dephosphorization of liquid iron.

Many experiments have been reported on the activity of phosphorous and oxygen in iron melt, including those by Bookey, Richardson and Welch[1] who suggested from the experiment of dephosphorization equilibrium with slag saturated with lime and tetracalcium phosphate that the phosphorous decreases the activity coefficient of oxygen, those by Pearson and Turkdogan[2] who measured the activity of oxygen dissolved in iron melts without slag and reported the value $e_0^{(P)}=\partial \log f_0^{(P)}/\partial[\%P]$ ($[\%P]\rightarrow 0$) $=-0.032$ as the interaction parameter, and those by Levenetz and Samarin[3] who studied the oxidation of phosphorous in liquid iron in a mixture of hydrogen/water-vapor and reported the value $e_0^{(P)}=-0.044$.

On the contrary, Dutilloy and Chipman[4] studied the effect of phosphorous on

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(1) J.B. Bookey, F.D. Richardson and A.J.E. Welch, J. Iron Steel Inst., **171** (1952), 404.
(2) J. Pearson and E.T. Turkdogan, J. Iron Steel Inst., **176** (1952), 19.
(3) N.P. Levenetz and A.M. Samarin, Doklady Akad. Nauk, SSSR, **101** (1955), 1089.
(4) D. Dutilloy and J. Chipman, Trans. AIME, **218** (1960), 428.

the activity of oxygen, using almost the same method as used by Pearson et al, and reported the positive value of interaction parameter, namely, $e_0^{(P)} = +0.07$.

Thus no reliable data is available on the effect of phosphorous on the activity of oxygen in iron melt. The effect, as represented by the interaction parameter given by above mentioned researchers, however, is too small, so that it is possible that the experimental errors and the differences due to the various methods of calculation may have considerable influence on the results.

In consideration of such possibility and for the purpose of examining the effect of temperature on the interaction parameter $e_0^{(P)}$, the following experiments were carried out.

II. Experimental procedure

The experimental technique was essentially that of equilibrating liquid iron-phosphorous alloy with a hydrogen/water-vapor mixture of known composition, and sucking the samples up with silica tube and analysing it for the phosphorous and oxygen contents. The experimental apparatus is shown in Figs. 1 and 2.

About 100g of iron-phosphorous alloy was first melted in an alumina crucible, and kept for about 30 minutes in the flow of hydrogen gas, and then a gaseous mixture of hydrogen/water-vapor and argon with 1 : 5 ratio of hydrogen to argon was introduced to the reaction chamber. The hydrogen and argon gases were passed through various purifing reagents to remove oxygen, carbon dioxide, hydrocarbons.

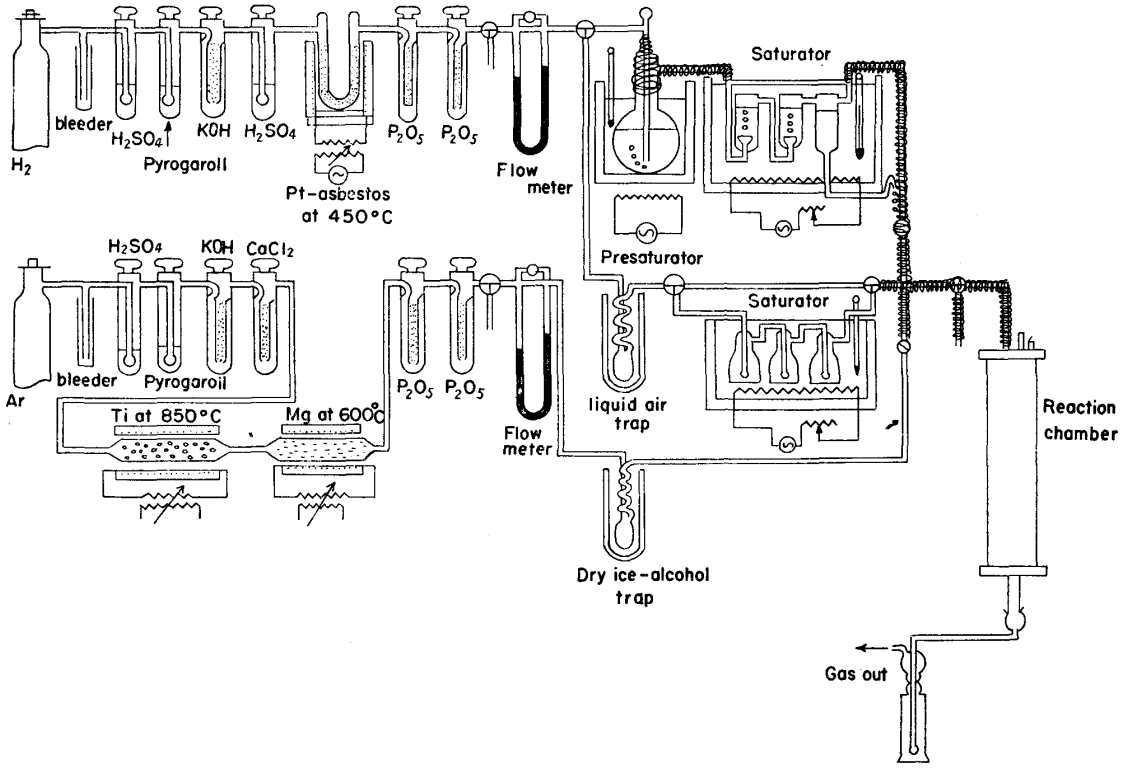

Fig. 1. Experimental apparatus.

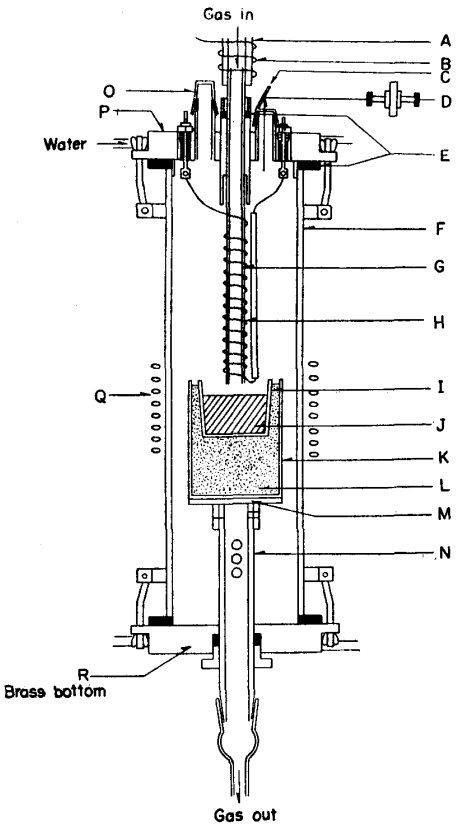

Fig. 2. Reaction chamber.

A Silicon rubber tube
B Resistance heater
C Mirror
D Optical pyrometer
E Gasket
F Quartztube
G Preheater tube (Alumina)
H Molybdenum wire
I Alumina crucible
J Liquid iron
K Alumina crucible
L Alumina powder
M Stainless steel disc
N Stainless steel tube
O Sampling window
P Brass head
Q Induction coil

It is known that thermal diffusion is almost eliminated by the addition of argon with 5: 1 ratio of argon to hydrogen, but for additional security, the gas mixture was introduced through a preheater kept at 1350°C ~ 1380°C before the contact with liquid iron-phosphorous alloy. An induction furnace was used for heating the samples and an optical pyrometer for measuring the temperature of the iron bath.

The temperature readings were corrected by a standard Pt-Pt · Rh (13%) thermocouple and the melting point of pure iron taken as 1535°C was used as a reference.

After attaining an equilibrium between gas mixture and liquid iron-phosphorous alloy, a silica tube was inserted to suck up samples, and the phosphorous and oxygen contents were determined by analysis.

The gravimetric method was used for determining phosphorous and the vacuum fusion method for oxygen content. The range of error in the latter method was usually not larger than ±0.0005%, within 0.01 ~ 0.04% oxygen content observed in the present study.

III. Experimental results

The experiment consisted of two series: In the first, the temperature of the melt and the oxygen potential in the gaseous phase were kept constant, but the concentration of phosphorous was varied to follow up the change in oxygen content; in the second, the oxygen potential in the gaseous phase was kept constant at $P_{H_2O}/P_{H_2}=0.074$, but the temperature of the melt was changed from 1540°C to 1585°C and 1625°C to determine the effect of the temperature on the interaction parameter $e_O^{(P)}$.

The results are shown in Table 1-(a), (b) and (c).

The reaction of hydrogen with oxygen dissolved in liquid iron and its equilibrium constant are as follows:

$$\underline{O} + H_2\,(g) = H_2O\,(g) \qquad (1)$$

Table 1–(a). Experimental results at 1585°C.

Run No.	[%P]	[%O]	logK'	log$f_0^{(P)}$
P1-1	0.10	0.0203	0.562	0.035
P1-1	0.10	0.0206	0.555	0.029
P1-1	0.10	0.0233	0.502	−0.025
P1-2	0.16	0.0205	0.558	0.031
P1-2	0.16	0.0210	0.547	0.020
P1-3	0.20	0.0194	0.581	0.055
P1-3	0.20	0.0218	0.530	0.004
P1-3	0.20	0.0227	0.513	−0.014
P1-4	0.58	0.0226	0.555	0.029
P1-4	0.58	0.0209	0.549	0.022
P1-5	0.80	0.0188	0.595	0.068
P1-5	0.80	0.0191	0.588	0.061
P1-6	1.09	0.0193	0.584	0.057
P1-6	1.09	0.0209	0.549	0.022
P1-7	1.50	0.0182	0.609	0.082
P1-7	1.50	0.0186	0.600	0.073
P1-8	1.86	0.0167	0.647	0.143
P1-8	1.86	0.0178	0.619	0.092
P1-9	2.40	0.0155	0.687	0.152
P1-9	2.40	0.0157	0.673	0.146
P1-9	2.40	0.0170	0.639	0.112
P1-9	2.40	0.0172	0.622	0.107

$p_{H_2O}/p_{H_2}=0.074$

Table 1–(b). Experimental results at 1540°C.

Run No.	[%P]	[%O]	LogK'	log$f_0^{(C)}$
P2-1	0.15	0.0140	0.723	0.035
P2-1	0.15	0.0152	0.687	0
P2-1	0.15	0.0156	0.676	−0.011
P2-2	0.35	0.0140	0.723	0.035
P2-2	0.35	0.0145	0.708	0.020
P2-2	0.35	0.0160	0.665	−0.022
P2-3	0.50	3 0140	0.723	0.035
P2-3	0.50	0.0152	0.687	0
P2-4	0.75	0.0135	0.739	0.042
P2-4	0.75	0..138	0.729	0.042
P2-5	1.00	0..139	0.726	0.039
P2-5	1.00	0.0141	0.720	0.003
P2-6	1.50	0.0140	0.723	0.035
P2-6	1.50	0.0145	0.708	0.020
P2-7	1.98	0.0135	0.739	0.042
P2-7	1.98	0.0138	0.729	0.042
P2-7	1.98	0.0141	0.720	0.033
P2-7	1.98	0.0145	0.708	0.020

$p_{H_2O}/p_{H_2}=0.074$

$$K = p_{H_2O}/p_{H_2} \cdot a_0 = p_{H_2O}/p_{H_2} \cdot [\%O] \cdot f_0' \qquad (2)$$

In the presence of dissolved phosphorous, the value of K is

$$K = p_{H_2O}/p_{H_2} \cdot [\%O] \cdot f_0' \cdot f_0^{(P)} \qquad (3)$$

where a_0 is the activity of oxygen in weight percent with infinitely dilute solution as standard, f'_0, the activity coefficient of oxygen in such a system, and $f_0^{(P)}$, the factor representing influence of phosphorous on the activity coefficient of oxygen.

According to the experimental result of one of authors and Omori[5] within

(5) K. Sanbongi and Y. Omori, Tetsu to Hagane, **47** (1961), 1324.

Table 1-(c). Experimental results at 1625°C.

Run No.	[%P]	[%O]	logK'	log$f_0^{(P)}$
P3-1	0.15	0.0249	0.473	0.0187
P3-1	0.15	0.0254	0.464	0.0103
P3-1	0.15	0.0263	0.449	−0.0048
P3-2	0.25	0.0237	0.494	0.0402
P3-2	0.25	0.0250	0.463	0.0173
P3-3	0.35	0.0229	0.509	0.0550
P3-3	0.35	0.0245	0.480	0.0257
P3-3	0.35	0.0250	0.463	0.0173
P3-3	0.35	0.0253	0.466	0.0120
P3-4	0.50	0.0240	0.489	0.0346
P3-4	0.50	0.0251	0.470	0.0154
P3-5	0.75	0.0232	0.504	0.0496
P3-5	0.75	0.0233	0.502	0.0645
P3-6	1.00	0.0217	0.533	0.0785
P3-6	1.00	0.0221	0.525	0.0704
P3-6	1.00	0.0223	0.521	0.0667
P3-6	1.00	0.0227	0.513	0.0588
P3-7	1.50	0.0210	0.535	0.0927
P3-7	1.50	0.0216	0.535	0.0806
P3-8	1.98	0.0230	0.507	0.0531
P3-8	1.98	0.0235	0.498	0.0438
	$p_{H_2O}/p_{H_2}=0.074$			

the range $p_{H2O}/p_{H2}=0\sim0.357$, f'_0 remains constant and $f'_0=1$. Therefore, if the temperature of the melt and the value of the gas ratio p_{H2O}/p_{H2} remains constant, the value of $f_0^{(P)}$ can be calculated by the ratio of oxygen content in pure iron melts and iron-phosphorous melts.

Theoretically, the oxygen content to be taken as the standard here should be either the observed value in a pure iron melts or the value calculated from the equilibrium constant, but in practice, the results from these two methods for estimating oxygen are subject to considerable errors, which may cause some discrepancy in the value of $f_0^{(P)}$ based on such a standard; so, in this study, the curve of [%O] versus [%P] was extrapolated to [%P→O] at which oxygen content was chosen as the standard.

The value of log $f_0^{(P)}$ thus obtained is shown in Table 1.

The apparent equilibrium constant K' is represented as follows:

$$K' = p_{H2O}/p_{H2} \cdot [\%O]$$

The relationship between [%P] and log $f_0^{(P)}$ from Table 1-(a) is shown in Fig. 3, which may be represented approximately by the following equation:

$$\log f_0^{(P)} = 0.06\,[\%P]$$

Therefore, the interaction parameter, $e_0^{(P)}=\partial \log f_0^{(P)}/\partial\,[\%P]$ ([%P]→O) is 0.06.

Similarly, the value $e_0^{(P)}=0.07$ is derived at 1625°C, but at 1540°C, experimental data show somewhat larger scattering than those at other experimental temperatures, $e_0^{(P)}$ covering the range of $0.05\sim0.07$.

The value of the interaction parameter $\varepsilon_0^{(P)}=\partial \ln\gamma_0^{(P)}/\partial N_P$, calculated from the

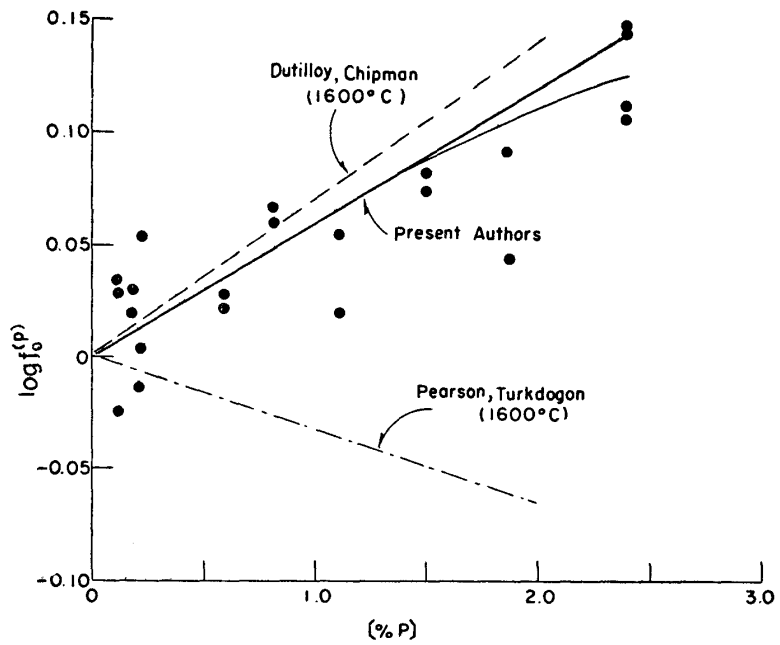

Fig. 3. Relation between [%P] and $\log f_0^{(P)}$ at 1585°C.

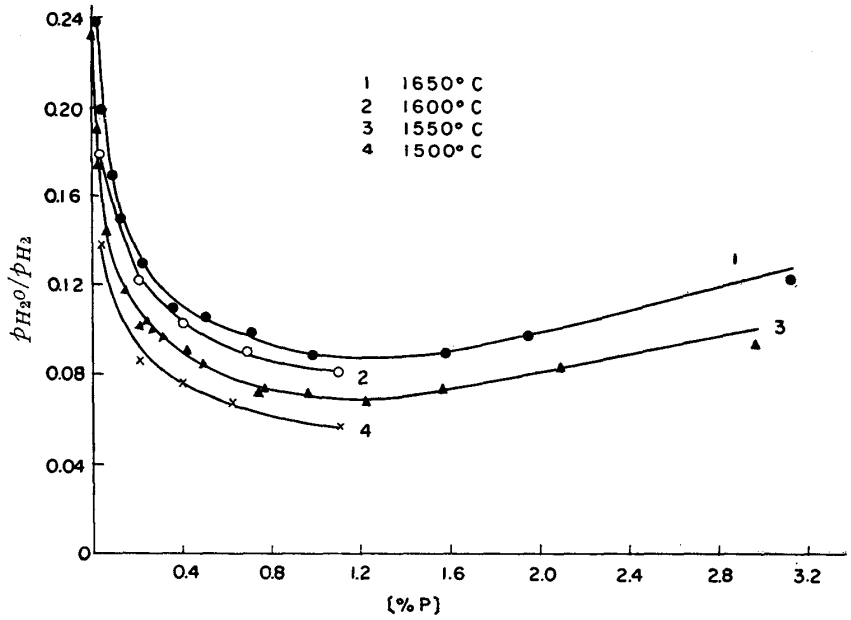

Fig. 4. Relation between [%P] and p_{H_2O}/p_{H_2} (N.P. Levenetz and A.M. Samarin).

results at 1585°C yields 7.7, where $\gamma_0^{(P)}$ represents the factor of the effect of phosphorous on the activity coefficient of oxygen as Raoult's Standard and N_P the mole fraction of phosphorous. In this system $\gamma_0^{(P)}$ is equal to γ_0 because γ'_0 is a unit, as already described.

By using Wagner's equation, the influence of oxygen content on the activity coefficient of phosphorous is calculated as follows:

$$e_p^{(0)} = \frac{16}{31} \times 0.06 = 0.03$$

III. Discussion of results

Dutilloy and Chipman[4] carried out comparative studies on the silica tube method and helium-quenching technique for sampling specimens for analyzing oxygen dissolved in iron, and recommended the former technique. Their results have been confirmed by some researchers. In this study, the silica tube method was used throughout for sampling, by which very preferable specimens could be obtained, and oxygen contents of different pieces of the same specimen were in good agreement.

The time required to establish equilibrium varied with different melting methods.

When the melt was held in hydrogen atmosphere for 30 minutes after melt down, a period of less than 1 hr was enough to establish equilibrium and a subsequent period of 2, 3 or 4 hrs caused no change in the equilibrium state.

Large numbers of works have been done on the activity of oxygen in liquid iron, but the effect of temperature on the activity of oxygen has been studied only in a few cases. In the studies by Dutilloy and Chipman[4] and Pearson and Turkdogan[2] on the interaction between oxygen and phosphorous in liquid iron, too, the measurements were carried out only at constant temperature or, if there are, the effect of temperature was disregarded in the calculation of the activity coefficient of oxygen.

In this study, measurements were made at three different temperatures for the purpose of obtaining some informations on the effect of temperature on the interaction between oxygen and phosphorous, in addition to following up the experimental results.

The present results show that the effect of temperature on the interaction parameter $e_0^{(P)}$ is very small and may be within the range of experimental errors.

Dutilloy and Chipman have criticized the experimental results on the solubility limit of phosphorous and oxygen in liquid iron reported by Levenetz and Samarin.

The present authors also performed some experiments under the oxygen potential up to $p_{H_2O}/p_{H_2}=0.23$ in order to check Levenetz and Samarin's results, but did not observe any slag formation throughout the range of $[\%P]=0\sim2$. This may also be confirmed from the experimental fact that the specimen melted in hydrogen atmosphere and brought to equilibrium with hydrogen/water-vapor gas mixture shows no significant difference in phosphorous content.

Summary

With a view to studying the interaction of oxygen and phosphorous in molten iron, the equilibrium measurement of iron-phosphorous alloy with a hydrogen water

vapor mixture was performed at 1540, 1585 and 1625°C.

The results show that phosphorous slightly increases the activity of oxygen dissolved in liquid iron, and the interaction parameter $e_0^{(P)}$ is about $+0.06$ at 1585°C.

Similar measurements were made at 1540°C and 1625°C to determine the effect of temperature on the activity of oxygen in iron melts, but $e_0^{(P)}$ remained in the range of $0.05 \sim 0.07$, showing little influence of temperature.

Acknowledgement

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